



# MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES

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## What? →

**We performed *ab initio* calculations of H<sub>2</sub>-Ar collisions and applied them to the simulation of the shape of anomalously broadened H<sub>2</sub> Q(1) line perturbed by Ar [1]**

- We performed highly accurate *ab initio* calculations of the three dimensional H<sub>2</sub>-Ar potential energy surface (PES).
- We calculated generalized cross sections for line broadening and shifting by solving the close-coupling (CC) equations.
- We used a hard-sphere approximation of the H<sub>2</sub>-Ar potential to describe velocity-changing collisions.
- We simulated the shape of H<sub>2</sub> line perturbed by Ar by solving the transport/relaxation equation for optical coherences [2,3].

## Why? →

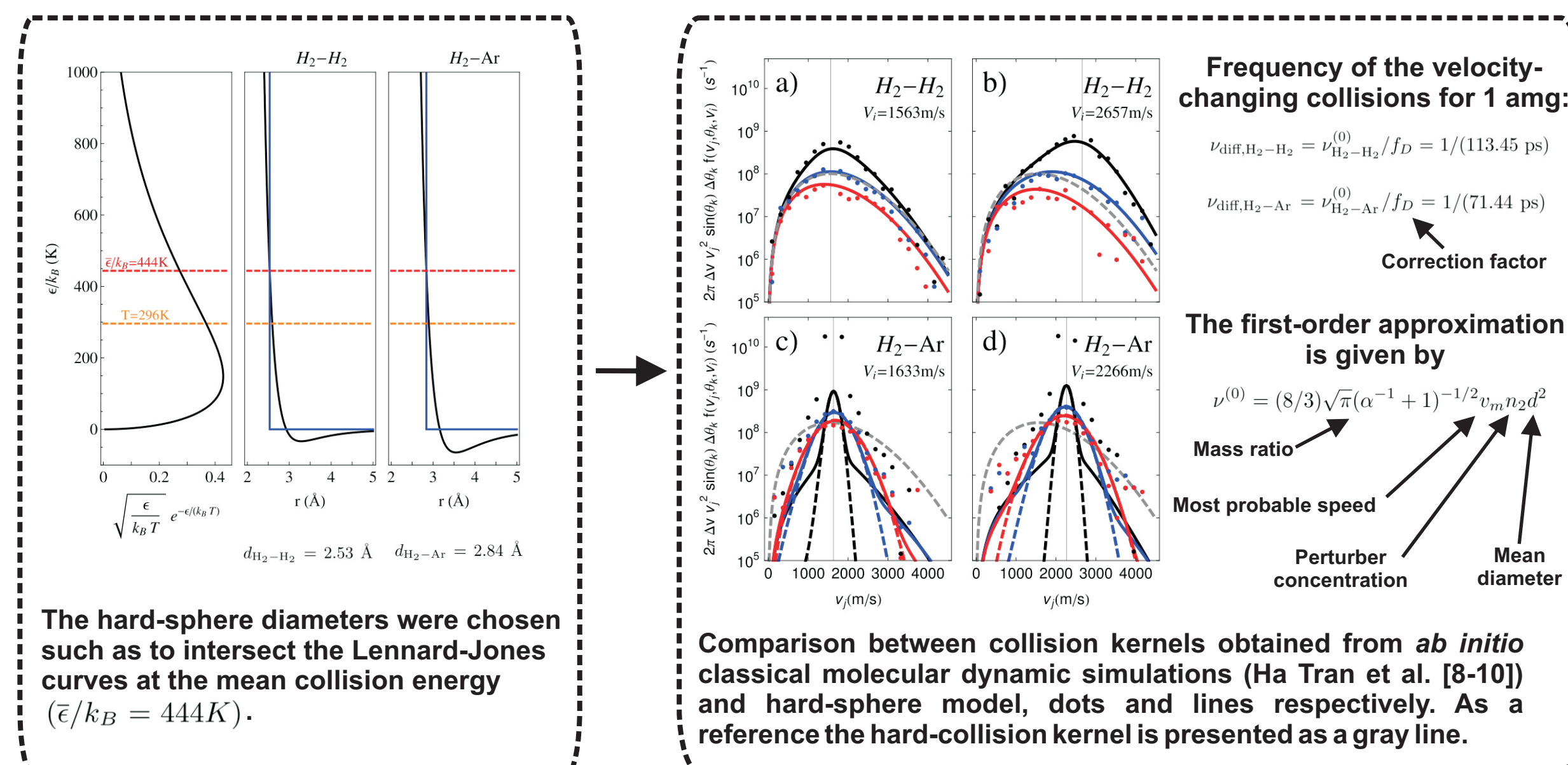
**For the H<sub>2</sub>/D<sub>2</sub>-Ar systems, fundamental discrepancies were reported [6,8] between experimental broadening coefficients [4,5] and thermally averaged close-coupling pressure broadening cross-sections**

- To understand the role of the velocity-changing collisions in the anomalous inhomogeneity in the Ar-broadening of the H<sub>2</sub> Q(1) line.
- The *ab initio* modeling of molecular line shape is essential to eliminate systematic errors in optical metrology based on molecular spectroscopy.

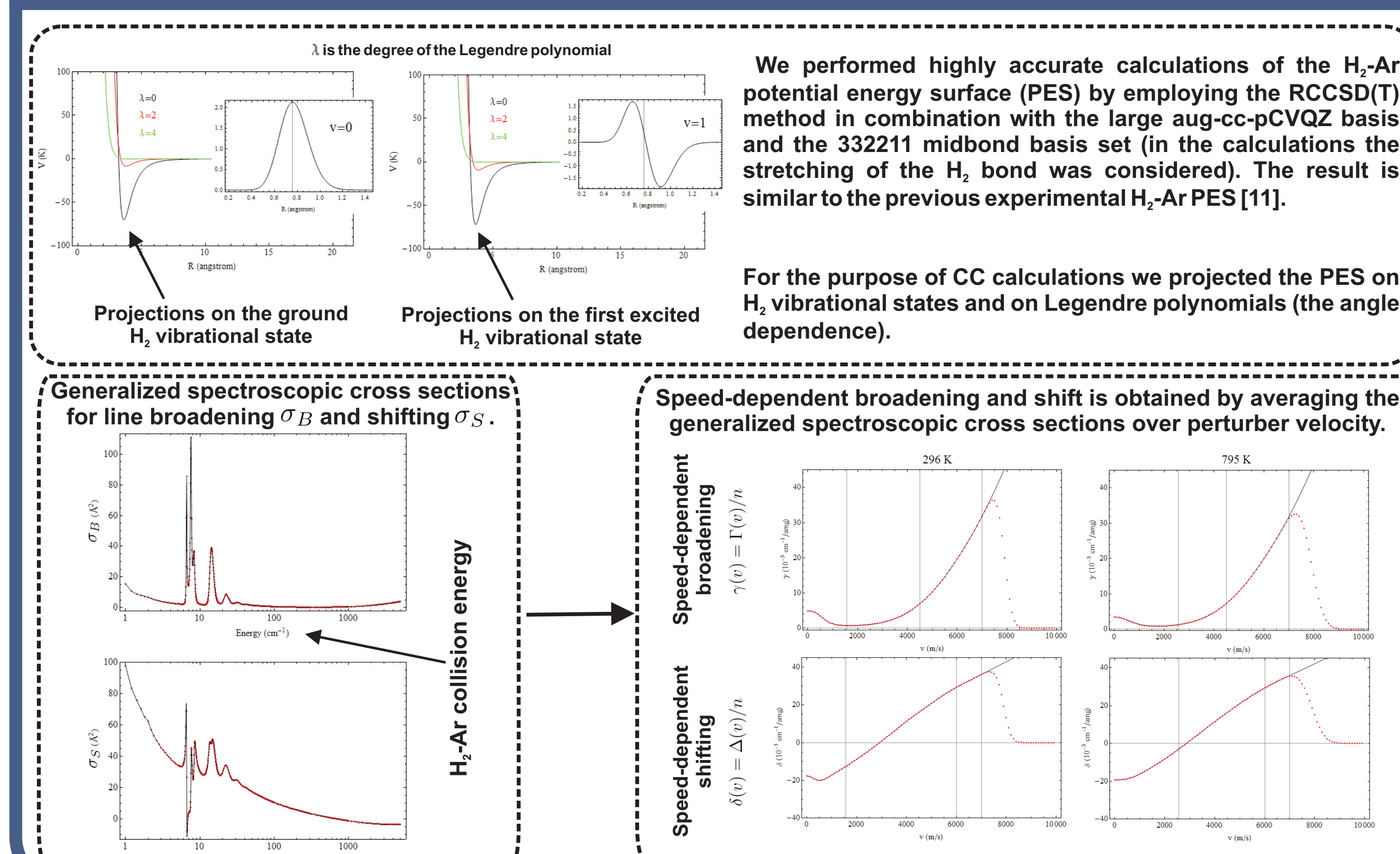
## How? ↓

### VELOCITY-CHANGING COLLISIONS

We demonstrated that, to properly describe the velocity-changing collisions, the H<sub>2</sub>-H<sub>2</sub> and H<sub>2</sub>-Ar potentials can be approximated by hard-sphere models [9].



### PHASE/STATE-CHANGING COLLISIONS



### REFERENCES

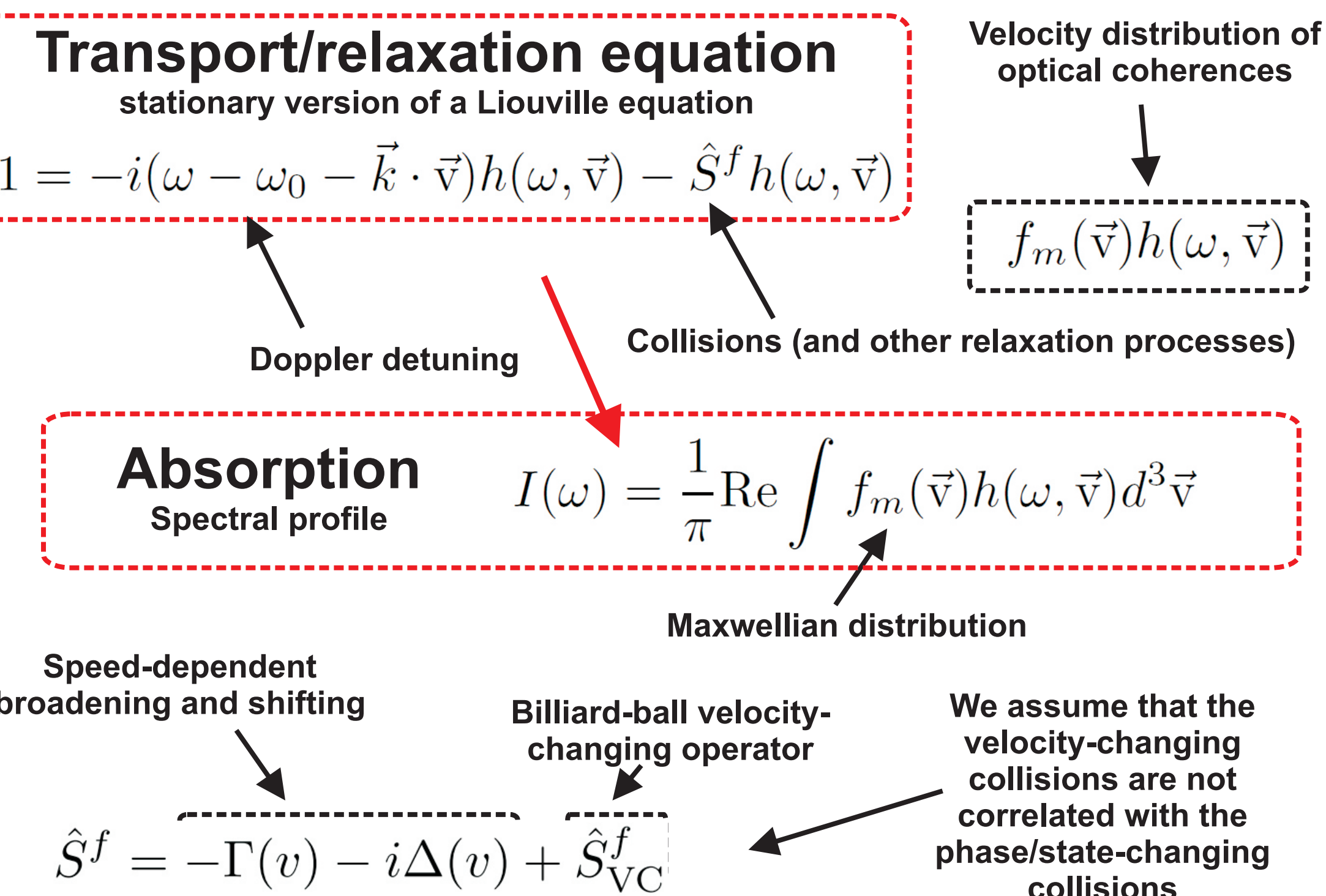
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### LINE-SHAPE MODEL

#### Speed-dependent billiard-ball profile [12]



### COMPARISON WITH EXPERIMENTAL DATA

Our approach eliminates fundamental discrepancies between simulated and measured broadening for H<sub>2</sub> Q(1) line perturbed by Ar [13]. We also compare the shapes of experimental lines with *ab initio* calculations.

